Theory of Local Electronic States in a Semi-Infinite Mixed Crystal

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A theory is presented to study the local electronic states in a semi-infinite mixed crystal, by extending the coherent potential approximation developed in the study for an infinite bulk crystal to the suitable one for a semi-infinite crystal. The effect of semi-infinity of a crystal is taken into account by the Sugakov's method in which the wave function of an electron is expressed in terms of the standing wave with nodes. The site dependent coherent potentials are introduced to calculate the local density of states in a semi-infinite mixed crystal. The appearance of the localized surface state is also discussed.

§1. Introduction

The existence of a surface in solids leads to interesting modifications of its properties. The surface states and its properties have been studied by many authors by various methods. An understanding of the surface electronic states is significant for the surface elementary excitations[1], chemisorption[2] or catalysis[3].

Recently, much interests have been focused on the electronic structures of a semi-infinite system, in connection with various phenomena taking place on the solid surface. Kalkstein and Soven introduced a Green's function formalism to study the surface states of a semi-infinite crystal. Their formalism is a extension of the localized perturbation method which was first introduced by Koster and Slater[5] in the study of a localized impurity state, and turn out to be a very powerful method by which both the surface and bulk properties of a semi-infinite crystal can be studied. The present authors discussed the principal features of surface exciton in molecular crystals using the cleaved crystal model[6] which is, in essence equivalent to Kalkstein and Soven method.

The another simple way to study electronic structures of a semi-infinite system was also given by Sugakov[7]. When we describe electrons by usual tight binding approximation in an infinite system, the eigenfunction of electrons is given by the Bloch function with translational symmetry of the underlying lattice. For a semi-infinite system, Sugakov took into account the effect of semi-infinity by expressing the eigenfunction in terms of the standing wave with nodes, in stead of the plain wave for an infinite system. Recently, we discussed a self-trapping of an electron in a semi-infinite system using the Sugakov method.[8]

Simple semi-infinite one dimensional models have deen widely used and played an important role in the development of the surface electronic state. They still serve as guides and are used as testing models before applications to realistic systems are made. News[9] has studied the chemisorption on the transition metal using a monatomic linear chain model. Levin and Davison[10] have made a detailed study of the surface states of a one dimensional ionic crystal. Foo and Johnson[11] calculated the local densities of states of the first three sites of a semi-infinite unsymmetric sp-band monatomic chain to study the Shockley surface state.

The electronic structures of a semi-infinite system have been thus widely studied but, to the author's knowledge, there have not been so investigated for a semi-infinite mixed crystal. Experiments[12] have been done to study the relation between the catalytic activity and the alloy composition of a clean surface of Cu-Ni alloy and show that the catalytic activity is sensitive to the surface electronic structures of alloy.

A theory for d-electrons at the surface of transition metal alloys is presented by Moran-Lopez et at.[13] They calculated the local density of states (LDS) at a clean and an adsorbate-covered surface of a random disordered alloy within the tight binding approximation using the continued fraction method. According to their results, only the LDS of the first two surface layers are changed with respect to the bulk denity of states. They also obtained the results that the LDS tend to narrow and to split into two peaks due to the existence of the surface. This result implies that the criterion which classifies the substitutional binary solid into two types, persistence and amalgamation types is changed at the surface. Ishida, Inoue and Matsubara[14] proposed a theory to treat the electronic properties of crystal with a plane or a linear chain surface on which two kinds of atoms are randomly distributed. Their theory is a combination of Kalkstein and Soven method and the coherent potential approximation.[15~18] They calculated the LDS in the case where two constituent atoms are distributed on a linear chain surface, not distributed in two dimensional bulk regions.

In this paper, we present a theory to treat the local electronic properties of a semi-infinite mixed crystal, extending the CPA developed for an infinite bulk crystal to a suitable one for a semi-infinite one dimensional crystal. In §2, we shall briefly review the bulk CPA and extend it to the case of a semi-infinite mixed crystal, where the effect of semi-infinity of a crystal is taken into account by the Sugakov method and the site dependent coherent potential is introduced. As explicitly shown in §2, introduction of the site dependent coherent potential in a semi-infinite mixed crystal is originated from the face thet the site diagonal configurationally averaged Green's function depends on site, whereas that of an infinite crystal is the same for all sites. The LDS of a present model is calculated in §3. Discussions are given in §4.

§2. Formulation

We consider a random mixed crystal, composed of two type atomic orbitals, A and B, characterized by the atomic excitation energy ε_A and ε_B, respectively. We assume that an electron is allowed to transfer between nearest neighbour sites with the trans-

fer energy J which is taken independent of site occupation.

Let us start from the usual tight binding Hamiltonian which is defined in terms of localized atomic orbital $|i\rangle$

$$H=\sum_i |i\rangle \varepsilon_i \langle i| + J\sum_{i\neq j} |i\rangle\langle j| \quad , \tag{2.1}$$

where the diagonal element represents random atomic level $\varepsilon_i=\varepsilon_A$ or ε_B depending on whether an atom A or B occupies the site i. The summations in eq.(2.1) extend over the sites of a semi-infinite crystal. Followed by the ordinary CPA, we separate eq.(2.1) into the translationally invariant part H_0 and the random contribution part H',

$$H=H_0+H', \tag{2.2}$$

where

$$H_0=\sum_i |i\rangle \varepsilon_V \langle i| + J\sum_{i\neq j} |i\rangle\langle j| \tag{2.3}$$

is the configurational average of the total Hamiltonian and describes a virtual crystal with a mean atomic excitation energy $\varepsilon_V=c_A\varepsilon_A+c_B\varepsilon_B$, c_A and $c_B(=1-c_A)$ being the concentration of the A and B atoms, respectively.
While

$$H'=\Delta\sum_i \eta_i |i\rangle\langle i| \quad , \tag{2.4}$$

where $\Delta=\varepsilon_A-\varepsilon_B$ is the difference in the atomic excitation energy and η_i is a random variable which takes c_B on A atom and $-c_A$ on B atom.

For a given concentrations of A and B atoms, the single particle Green's function is defined as

$$g(z)=(z-H)^{-1} \tag{2.5}$$

The system is then characterized by the configurationally averaged Green's function

$$G(z)=\langle g(z)\rangle_{aV}=\langle (z-H)^{-1}\rangle_{aV} \tag{2.6}$$

The ordinary CPA replaces $\langle g(z)\rangle_{aV}$ by the Green's function for the effective "periodic" medium;

$$G(z)=(z-H_{eff})^{-1} \quad , \tag{2.7}$$

where the effective Hamiltonian H_{eff} which describes the averaged crystal is defined as

$$H_{eff}=H_0+\sum_i \sigma_i(z) \quad , \tag{2.8}$$

where σ_i is the coherent potential of the mixed crystal with respect to the virtual crystal. As well known the effective medium described by σ is determined by setting the averaged scattering potential $\langle t_i\rangle_{aV}(=c_A t_A+c_B t_B)$ of a single site immersed in the medium equall zero. This condition leads to a self-consistent equation which determines the coherent potential[19];

$$\sigma_i=(\Delta c_B-\sigma_i)\langle i|G(z)|i\rangle(\Delta c_A+\sigma_i) \quad . \tag{2.9}$$

For an infinite crystal with translational symmetry, the site diagonal Green's function $<i \mid G(z) \mid i>$ in eq. (2.9) can be displayed in the form.[15]

$$<i \mid G(z) \mid i> = f(z-\varepsilon_V-\sigma) , \qquad (2.10)$$

where

$$f(z) = \frac{1}{N} \sum_k \frac{1}{z-2J\cos ka} . \qquad (2.11)$$

In this case we have $\sigma_i = \sigma$ for all sites and then eq. (2.9) reduced to the equation which determines the site independent coherent potential of an infinite mixed crystal. In an semi-infinite crystal, the effective Hamiltonian thus posseses the full translational symmetry. Conceptually, H_{eff} can be throught of as the Hamiltonian of the effective periodic medium.

On the otherhand, coherent potential of a semi-infinite crystal is essentially site dependent due to the existence of a free end or a surface. The origin of the site dependent (in one dimension) or plane dependent (in three dimension) coherent potential, in other words, of the difference from the the bulk CPA is easily understood as follows. For an infinite crystal with $\sigma_i = \sigma$ for all sites, the eigenfunction of the effective Hamiltonian given by eq. (2.8) is given by the Bloch function

$$\mid k> = \frac{1}{\sqrt{N}} \sum_i \exp(ikR_i) \mid i> , \qquad (2.12)$$

and the site diagonal Green's function is given by eq. (2.10) using eq. (2.12).

For a semi-infinite crystal, the eigenfunction of the virtual crystal of which Hamiltonian is given by eq. (2.3) is not given by eq. (2.12) due to the existence of the free end. The simple form of the eigenfunction of a semi-infinite one dimensional crystal was given by Sugakov[7] as follows;

$$\mid k> = \frac{1}{\sqrt{N}} \sum_i a_i(k) \mid i> , \qquad (2.13)$$

where the site dependent coefficient $a_i(k)$ is given by the standing wave*

$$a_i(k) = \sqrt{2}\sin(kia) , \qquad (2.14)$$

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* For a semi-infinite three dimensional crystal, the coefficient is expressed, employing the usual periodic condition on the wave function parallel to the surface plane, as follows;

$$a_i(k) \rightarrow a_i(k_\perp, k_{/\!/}) = \sqrt{2}\sin(k_\perp l a_3)\exp(ik_{/\!/} n)$$

where $k_\perp$ and $k_{/\!/}$ are the wave vector perpendicular and parallel to the crystal plane and site $R_i = l a_3 + n$, $n = n_1 a_1 + n_2 a_2$, $l = 1, 2, \cdots N_3$, $n_{1,2} = 0, \pm 1, \cdots, N_{1,2}/2$.

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which, of course, satisfies the orthonormality conditions

$$\sum_i a_i^*(k)a_i(k') = \delta_{k,k'} \quad , \qquad \sum_k a_i^*(k)a_{i'}(k) = \delta_{i,i'} \quad .$$

Using eqs. (2.13) and (2.14), we obtain the site dependent Green's function which satisfies the equation

$$(E-H_0)G_0 = 1 \quad , \tag{2.15}$$

as follows;

$$G_0(i, i'; E) = \frac{1}{N}\sum_k \frac{a_i^*(k)a_{i'}(k)}{E-2J\cos(ka)} \quad . \tag{2.16}$$

The sum over k in eq. (2.16) can be converted to an integral over $ka=\theta$;

$$\frac{1}{N}\sum_k \rightarrow \frac{1}{2\pi}\int_{-\pi}^{\pi} d\theta \quad .$$

The site dependent Green's function G_0 is then given as

$$G_0(i, i'; E) = \frac{1}{2J\sqrt{E^2-1}}[\{f(E)\}^{|i-i'|} - \{f(E)\}^{|i+i'|}] \quad , \tag{2.17}$$

where the energy E is measured in unit of half band width $2J$ and $f(E)=E-\sqrt{E^2-1}$ $(E>1)$, $E+\sqrt{E^2-1}$ $(E<-1)$, $E-i\sqrt{1-E^2}$ $(|E|<1)$.

From eq. (2.17), the site diagonal Green's function is given by

$$G_0(i, i; E) = \frac{1}{2J\sqrt{E^2-1}}[1-\{f(E)\}^{2i}] \quad . \tag{2.18}$$

One can notice from eq. (2.18) that the site diagonal Green's function depends on site.* Thus the site dependent Green's function G which satisfies the equation

$$(E-H_{eff})G = 1 , \tag{2.19}$$

is, in general, dependent on the site dependent coherent potential σ_i $(i=1, 2, \ldots)$. The self-consistent equation (2.9) consequently leads to infinite coupled equations which are intractable. It may be reasonable to assume that the site dependent coherent potential approaches to the bulk coherent potential, well into the interior regions of crystal.
The question will arise how rapidly does the effect of a free end vanish as one recedes from a free end. Moran-Lopez *et al.*[13] calculated the LDS of the first three sites in a semi-infinite disordered alloy. They showed that the effect of a free end is pronounced only in the first site and the LDS at the second or third site is not so different from that in the bulk regions, In this regard, it should be mentioned here that the

* For semi-infinite three dimensional crystal, eq. (2.18) depends on the crystal plane, deing independent on site in a given plane.

behavior of the LDS at a given site is govered by the detailed energy variation of the site dependent coherent potential which is implicit in the form of the site dependent Green's function given by eq. (2.18). The Green's function $G_o(i, i; E)$ rapidly approaches to the bulk Green's function with an increase of i. Recently, we calculate the localized energy of an electron due to its interaction with one site lattice deformation in a semi-infinite one dimensional cryrtal.[8]*

We find that the localized energy at the first site or. at most, at the second site differs from that interior bulk sites. We therefore assume that the existence of a free end affects on the local electronic property at a free end, in order to make the problem to be manageable.

We then approximate the effective Hamiltonian (2.8) as the following simple form;

$$H_{eff} = H^{o}_{eff} + V \tag{2,20}$$

$$H^{o}_{eff} = \sum_{i} |i\rangle(\varepsilon_V + \sigma_b)\langle i| + J\sum_{i \neq j} |i\rangle\langle j|, \tag{2.21}$$

$$V = (\sigma_f - \sigma_b)|1\rangle\langle 1|, \tag{2.22}$$

where σ_b, σ_f are the bulk and free end coherent potentials, respectively. Here, we approximate the site dependent coherent potential into the site independent bulk one for all interior sites and the free end one. The difference in the coherent potential, given by eq. (2.22) is treated as the local perturbation which acts on a semi-infinite crystal.

Let G_o and G be the corresponding Green's function of H^{o}_{eff} and H_{eff}, respectively. The Green's function G is given in terms of G_o as fllows;

$$G = G_o + G_o V G ,$$

or in an explicit form as

$$G(i, i') = G_o(i, i') + \sum_{j,k} G_o(i, j)V(j, k)G(k, i') . \tag{2.23}$$

From eqs. (2.22) and (2.23), site diagonal Green's function of a semi-infinite mixed crystal is expressed as

$$G(i, i) = G_o(i, i) + \frac{G_o(i, 1)(\sigma_f - \sigma_b)G_o(1, i)}{1-(\sigma_f - \sigma_b)G_o(1, 1)} . \tag{2.24}$$

Under the above simplified approximation, the self-consistent equation (2.9) reduces to two coupled equations which determine σ_b and σ_f;

$$\sigma_b = (\Delta c_B - \sigma_b)G_b(E)(\Delta c_A + \sigma_b) , \tag{2.25}$$

$$\sigma_f = (\Delta c_B - \sigma_f)G_f(E)(\Delta c_A + \sigma_f) , \tag{2.26}$$

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* This problem is formally analogous to the low concentration limit of the present system, where the CPA is reduced to the single site impurity problem.

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where the Green's function at a free end is obtained from eq. (2.24), putting i=1,

$$G_f(E) = \frac{1}{G_0(1,1;E)^{-1}-(\sigma_f-\sigma_b)} \quad , \tag{2.27}$$

and $G_0(1,1;E)$ is given by eq. (2.18).
The bulk Green's function $G_b(E)$ which is independent on sites issgiven by

$$G_b(E) = \frac{1}{2J\sqrt{E^2-1}} \quad . \tag{2.28}$$

The bulk coherent potential σ_b is first calculated from the usual CPA equation (2.25) by making use of eq. (2.28). The calculated σ_b is then inserted into eq. (2.27) and we finally obtain σ_f from eq. (2.26). The solutions of eqs. (2.25) and (2.26) are obtained by numerical calculations. Before performing numerical calculations, we mention to some limitting cases.

In the amalgamation limit where the band width is very large compared with difference in the atomic excitation energy, i.e., $\Delta/2J \ll 1$, σ_b and σ_f are given by

$$\sigma_b(E) = c(1-c)\Delta^2[G_b(E)]_{\sigma_s\to 0} \quad ,$$

$$= c(1-c)\Delta^2\frac{1}{\sqrt{(E-c\Delta)^2-1}} \quad , \tag{2.29}$$

and similarly

$$\sigma_f(E) = 2c(1-c)\Delta^2\frac{1}{E-c\Delta+\sigma_b-\sqrt{(E-c\Delta-\sigma_b)^2-1}} \tag{2.30}$$

where the energy is measured relative to ε_B in unit of 2J and $c=c_A$. In the opposite limit ($\Delta \gg 1$), i.e., the persistent limit where the energy band is split into two bands, approximately corresponding to the individual constituents, $G_b(E)$ and $G_f(E)$ are given by

$$G_b(E) = \frac{1}{E-c\Delta-\sigma_b} \quad , \tag{2.31}$$

$$G_f(E) = \frac{1}{G_b(E)^{-1}-\sigma_f+\sigma_b} = \frac{1}{E-c\Delta-\sigma_f} \tag{2.32}$$

In that limit, one has

$$\sigma_f(E) = \sigma_b(E) = \frac{c(1-c)\Delta^2}{E-(1-c)\Delta} \tag{2.33}$$

In the persistent limit where the transfer energy vanish, the system loses the meaning of its semi-infinity and therefore two different coherent potentials coincide with each other. From eqs. (2.31)-(2.33), we obtain

$$G_b(E) = G_f(E) = \frac{c}{E-\Delta} + \frac{1-c}{E} , \tag{2.34}$$

as is expected in the zero transfer limit.

In the low concetration limit ($c \to 0$), the CPA reduces to the single impurity problem. Retaining terms up to the order c in eq.(2.25), we obtain

$$\sigma_b(E) = \frac{c\Delta^2}{\sqrt{E^2-1}-\Delta} \quad . \tag{2.35}$$

The pole of eq.(2.35) gives the energy of the localized impurity level. One can easily find from eq.(2.35) that there always appears the localized impurity state for any small values of Δ. This is a common property of an infinite one dimensional crystal. On the otherhand, free and coherent potential in this limit is given by

$$\sigma_f(E) = \frac{1}{(E+\sigma_b-\sqrt{(E-\sigma_b)^2-1})^{-1}-2\Delta} \quad . \tag{2.36}$$

§3. Local Density of States at a Free End.

In general case, two coupled equations (2.25) and (2.26) are rewritten as following ones;

$$2(E-\Delta+c\Delta)\sigma_b^3 + \{\Delta^2(5c^2-6c+1) + 2c\Delta E - E^2 + 1\}\sigma_b^2 + 2\Delta^3 c(1-c)(1-2c)\sigma_b + \Delta^4 c^2(1-c)^2 = 0 \ , \tag{3.1}$$

$$\{4(\Delta-c\Delta-E)(\Delta-2c\Delta-\sigma_b)+1\}\sigma_f^2 + 4\{\Delta^2 c(1-c)(2\Delta-3c\Delta-E-\sigma_b)\}\sigma_f + 4\Delta^2 c^2(1-c)^2 = 0 \ . \tag{3.2}$$

We first solve eq.(3.1) and insert σ_b into eq.(3.2). The cubic equation (3.1) has either three real roots or one real and two complex roots as functions of E, c and Δ. Only a complex root with a positive imaginary part is meaning because that the bulk density of states diverses at the energy where the imaginary part of σ_b ($=\sigma_b^I$) vanishes. We then solve the quadratic equation (3.2) with complex coefficients. In Fig. 1, we show σ_b^I and σ_f^I as a function of Δ, where c is fixed as 0.1.

The bulk density of states for one dimensional mixed crystal is given by

$$\rho_b(E) = \frac{1}{\pi}\mathrm{Im}\{G_b(E)\}$$

$$= \frac{\sqrt{\sqrt{\{(E-c\Delta-\sigma_b^R)^2-\sigma_b^{I2}-1\}^2+\{2\sigma_b^I(E-c\Delta-\sigma_b^R)\}^2}-(E-c\Delta-\sigma_b^R)^2+\sigma_b^{I2}+1}}{\pi\sqrt{\{(E-c\Delta-\sigma_b^R)^2-\sigma_b^{I2}-1\}^2+\{2\sigma_b^I(E-c\Delta-\sigma_b^R)\}^2}} \tag{3.3}$$

where σ_b^R is the real part of σ_b.

The bulk density of states $\rho_b(E)$ shown in Fig. 2 are those as expected. Detailed discussions were given for infinite one dimensional mixed crystal by Butler[19] and White and Economou.[20] We then do not repeat it here.

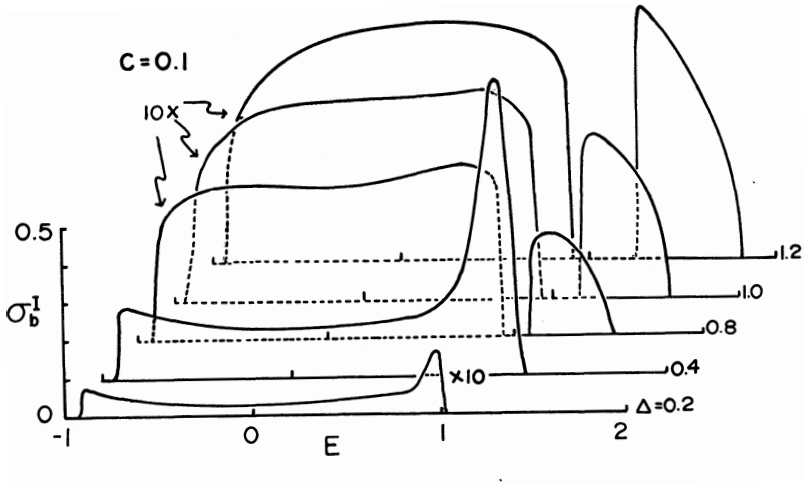

Fig. 1(a) Imaginary part of the bulk coherent potential for c=0.1 and Δ=0.2, 0.4, 0.8, 1.0 and 1.2.

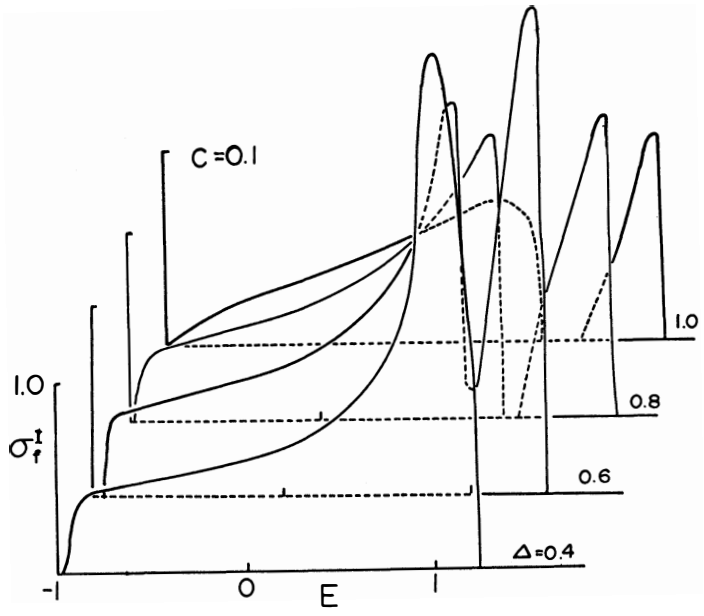

Fig. 1. (b)Imaginary part of the coherent potential at the free end for c=0.1 and Δ=0.4, 0.6, 0.8 and 1.0.

The local density of states (LDS) at the free end is given by

$$\rho_f(E) = \frac{1}{\pi}\mathrm{Im}[G_f(E)] \quad , \tag{3.4}$$

$$= \frac{1}{\pi}\mathrm{Im}\left[\frac{1}{\sqrt{E-c\Delta+\sigma_b-2\sigma_f-\sqrt{(E-c\Delta-\sigma_b)^2-1}}}\right]$$

In the energy region where the bulk density of states does not vanish, i.e., $\sigma_b^I \neq 0$, the vanish, forming the band state, and is given by

$$\rho_f(E) = \frac{1}{\pi} \frac{(2\sigma_f^I - \sigma_b^I + Y)}{(E - c\Delta + \sigma_b^R - 2\sigma_f^R - X)^2 + (2\sigma_f^I - \sigma_b^I + Y)^2} \quad , \qquad (3.5)$$

where

$$X + Y = \sqrt{\{(E - c\Delta - \sigma_b^R)^2 - \sigma_b^{I2} - 1\}^2 + \{2\sigma_b^I(E - c\Delta - \sigma_b^R)\}^2},$$

$$XY = 2\sigma_b^I(E - c\Delta - \sigma_b^R)$$

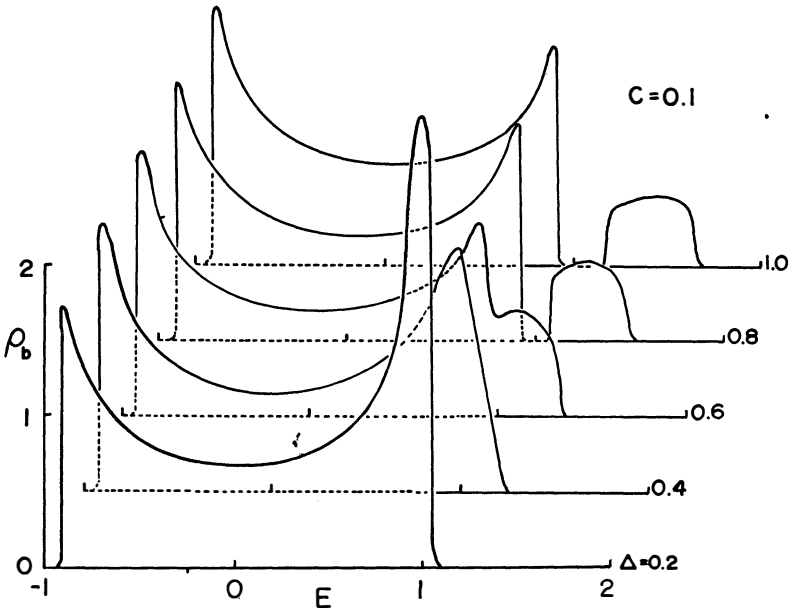

Fig. 2 Bulk density of states for one dimensional mixed crystal for c=0.1 and Δ=0., 0.4, 0.6, 0.8 and 1.0.

From eq. (3.5), we find that LDS vanishes when σ_b^I and ρ_f^I simultaneously become zero. As shown in Fig. 1, σ_b^I and σ_f^I simultaneously become zero as functions of c and Δ. This result implies that the boundary between the persistence and the amalgamation type in the LDS is same as that in the bulk density of states, within the model presented here.

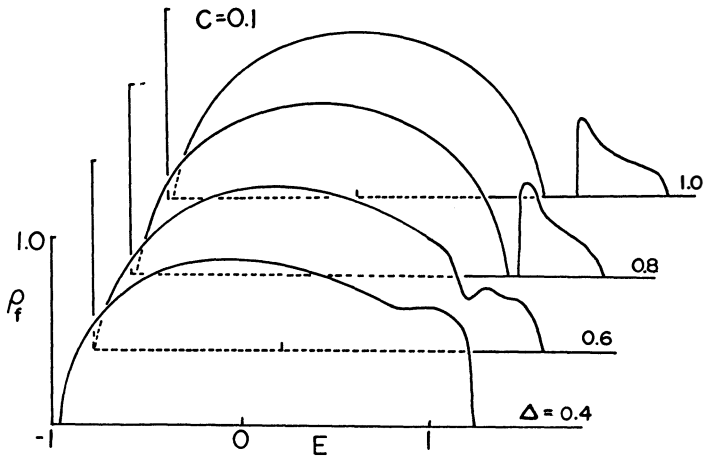

Fig. 3 Local density of states at the free end of a semi-infinite one dimensional mixed crystal for c=0.1 and Δ≠0.4, 0.6, 0.8 and 1.0.

The LDS is shown in Fig. 3. where parameters are same as Fig. 2, Besides the LDS which shows the band state, we expect the appearance of the localized surface state in the energy region where $\sigma_b^I = 0$.

The self-consistent equation (2.26) is rewritten as

$$G_f(E) = \frac{1}{G_f(E)^{-1} - (V_i - \sigma_f)} \quad , \tag{3.6}$$

where the impurity potential V_i takes $(1-c)\Delta$ for $i=A$ and $-c\Delta$ for $i=B$ and $\langle \cdots \rangle$ is an ensemble average over all distribution of the two atom. Inserting eq. (2.27) to the right hand side of eq. (3.6), we obtain

$$G_f(E) = \frac{1}{G_0(l, l; E)^{-1} - (V_i - \sigma_b)} \quad . \tag{3.7}$$

One finds from eq. (3.7) that $\mathrm{Im}[G_f(E)]$ do not vanish in the energy region where $\sigma_b^I \neq 0$ and becomes zero for $\sigma_b^I = 0$, except at the energy which gives the real pole of eq. (3.7). The localized surface state is thus expected in the energy region where the bulk density of states vanishes. The energy of surface states is obtained fqom the equation

$$G_0(l, l; E)^{-1} - (V_i - \sigma_b) = 0 . \tag{3.8}$$

It should be mentioned here that surface state do not appear in pure semi-infinite crystal within the model treated here. From eq. (3.8), we obtain the energy of surface state as

$$E_s^i = c\Delta + V_i - \frac{1}{4(\sigma_b - V_i)} \quad ,$$

i. e.,

$$E_s^A = \Delta - \frac{1}{4\{\sigma_b - (1-c)\Delta\}} \quad , \tag{3.9}$$

$$E_s^B = -\frac{1}{4(\sigma_b + c\Delta)} \quad . \tag{3.10}$$

Equations (3.9) and (3.10), of course, satisfy the dual symmetry. Equation (3.9) is obtained by replacing E, c and Δ by $E-\Delta$, $1-c$ and $-\Delta$, respectively in eq. (3.10). Here the following condition must be satisfied for the appearance of the surface state;

$$|\sigma_b - V_i| > 0.5 \quad . \tag{3.11}$$

The surface state appears as the δ-function in the LDS;

$$\rho_f^s = I_s^i (E - E_s^i) , \quad i=A, B \tag{3.12}$$

where the intensity of the δ-function I_s^i is given by

$$I_s^i = \frac{c}{2}\left[1 - \frac{1}{4\{\sigma_b - (1-c)\Delta\}^2}\right]$$

$$I_s^i = \frac{(1-c)}{2}\left[1 - \frac{1}{4(\sigma_b + c\Delta)}\right] \quad .$$

The real bulk coherent potential σ_b appearing in eqs. (3.9) and (3.10) is, of course, the function of E. Then we must calculate the self-consistent energy whicn satisfies eqs. (3.9) and (3.10). Under the various conditions for the appearance of the surface state, i.e., $|E-c\Delta-\sigma_b|>1$, $|\sigma_b-V_i|>0.5$ and $\sigma_b^I=0$, the surface state appears in the limited region $\Delta-0.5<E_s^A<\Delta+0.5$, $-0.5<E_s^B<0.5$ for given c and Δ, as schematically shown in Fig. 4. We performed numerical calculation to obtain the energy of the surface state. The results are shown in Fig. 5, where the dual symmetry relation for the surface state $E_s^A(1-c)-\Delta=E_s^B(c)$ is satisfied.

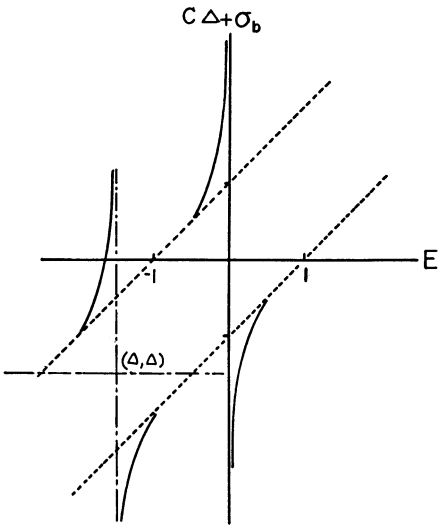

Fig. 4 Possible energy region which satisfies eqs. (3.9) and (3.10) as a function of $c\Delta+\sigma_b$. The dashed line is given by the equation $E-c\Delta-\sigma_b=\pm 1$

We find that the surface state lies in the midgap region, i.e., the surface state appears in the persistence type crystal where both the LDS and the bulk one are split into two bands. It is pointed out here that the surface state in mixed crystal appears for small impurity concentration and when the atomic excitation energy of an impurity atom is very small compared with that of a host atom. In Fig. 6, we show the LDS for $c=0.9$ and $\Delta=0.6$, 1.0 and 1.6. The surface state with the energy E due to B-atom impurities appears in the midgap for $\Delta=1.6$. The corresponding bulk density of state is also shown in Fig. 6.

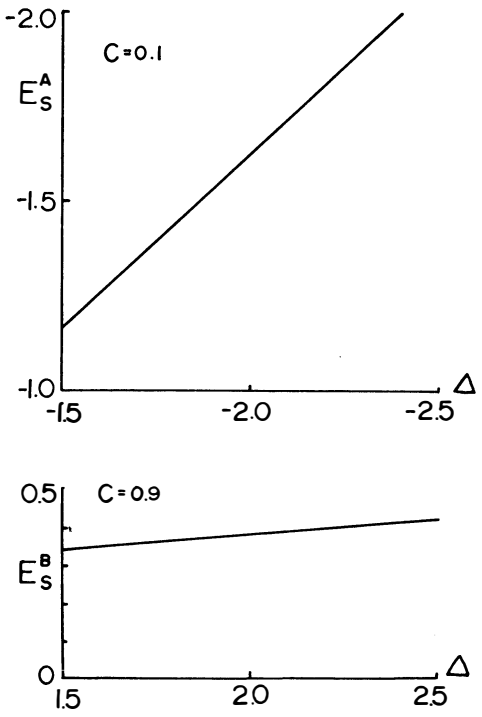

Fig. 5 Energy of the surface state as function of c and Δ.

§ 4. Discussions.

We have shown a simple theory to treat the local electronic properties of a semi-infinite mixed crystal. The method presented here is a extension of the CPA developed in an infinite bulk crystal to a suitable form in a semi-infinite crystal. We introduced the site dependent coherent potential which arises from the fact that the site diagonal configurationally averaged Green's function depends on sites.

We calculated the LDS for a semi-infinite mixed crystal, which is influenced by

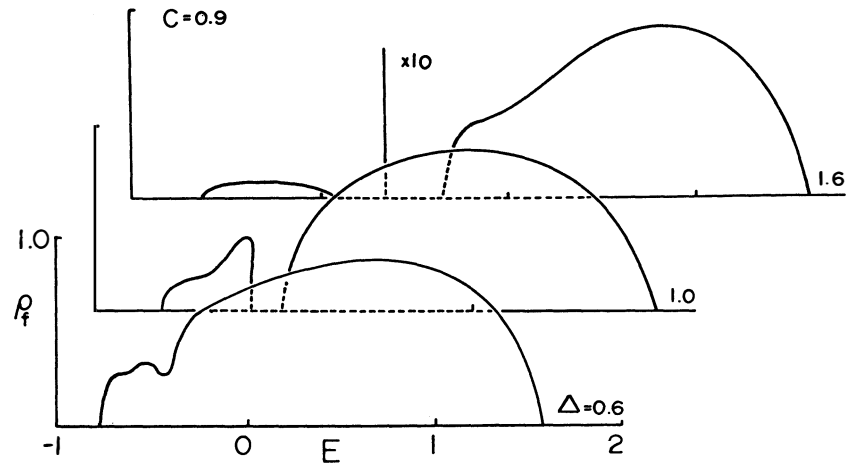

Fig. 6(a) Local density of states at the free end for c=0.9 and Δ=0.6, 1.0 and 1.6. A surface state appears at the midgap for Δ=0.6.

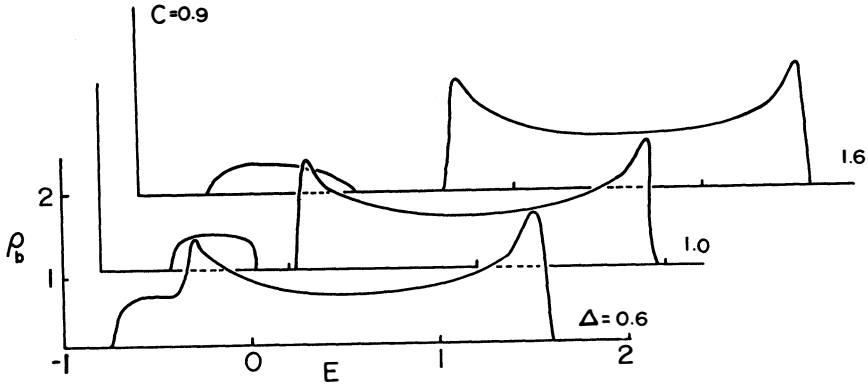

Fig. 6(b) Bulk density of states for the same parameter as Fig. 6(a).

the property of the bulk density of states. The principal shapes of the LDS in a semi-infinite pure crystal, (they correspond to the case c=0 or 1), agree with that calculated by Foo and Johnson[11], Bose and Foo.[21] Within a simple model we point out that the boundary between the persistence and the amalgamation type in the LDS is the same as that in the bulk one.*

We also showed that the surface state, which is originated from the co-operative effect of semi-infinity of crystals and of the impurity potential, appears in the midgap between two separated bands, i. e., in the persistence type mixed crystal. The appearance of the surface state in mixed crystal was not discussed by Moran-Lopez et al.,[13] because they mainly studied the surface electronic states of the amalgamation type

* A narrowing of energy bands at the surface suggested by Moran-Lopez et al.[13] is not observed in the photoemission study of the surface electronic states of Cu-Ni alloys.[22]

crystal. The surface electronic states have significant effects on various phenomena at the surface of mixed crystal, such as the order-disorder transition[23] or the chemisorption properties.[24] Foo and Davison[25] discussed the effect of the surface state on the chemisorption of the sp-hybrid semi-infinite monatomic chain and suggested that the surface state appearing in the bandgap strengthens the chemisorption bond.

The present model is very primitive in several respects the existence of a free end is assumed to affect on the LDS at a free end. The LDS characterized by σ_f depends on the bulk electronic properties through the σ_b-dependence of σ_f. The simplified assumption is removed by extending the site dependent coherent potential to more interior sites. The present formulation is easily extended to a semi-infinite three dimensional crystal, by replacing the energy E in eq.(2.16) by $E-2J(\cos k_x a+\cos k_y a)$ and performing the summation over k_x and k_y, and k_y being the wave vector parallel to the surface. In this case, the coherent potential depends on crystal planes and is the same for all sites in a plane. The results may be, however, different from that discussed here because of the different form of the site diagonal Green's function.

As a final, we mention to the effect of the inhomogeneous distribution of two constituent atoms near the surface (surface segregation). Recent experimental results show that the concentration ratio near the surface is different from that in the bulk regions. The surface electronic properties are also strongly influenced by the surface composition since the surface atoms retain much of their atomic character. The presnt theory incorporates its effect by introducing the plane dependent concentration c_l and defining the CPA equation as

$$\langle t_l \rangle = c_l t_A + (1-c_l) t_B$$

The effect of the inhomogeneous distribution on the surface electronic properties will be studied in the followin paper.

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